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DEPENDENCE OF RELATIVE QUANTUM YIELD OF LUMINESCENCE OF ZnO ON LENGTH OF EXCITATION WAVE

F. I. Vergunas and F. F. Gavrilov

ABSTRACT

The authors investigate the dependence of yield of spontaneous luminescence of ZnO on the length of excitation wave. The nature of this dependence for most phosphor crystals has not yet been adequately established, due to the difficulty of measuring absorption in powders and the existence for most such phosphor crystals of prolonged luminescence which may be a source of errors in measuring the yield of spontaneous luminescence. Zinc oxide is used because it offers better measurements of the dependence in question than other phosphor crystals. Absorption was determined for ZnO films 10^{-4}--10^{-5} cm thick by measuring the attenuation in the light passing through them. The luminescence of zinc oxide, according to measurements of its electrical and optical properties, is attributed to the movement of electrons of the local level of atoms of the excess zinc to the primary zone.

INTRODUCTION

This investigation had as its purpose determining the dependence /1273* of yield of spontaneous luminescence of ZnO on the length of excitation wave. The work was done because the nature of this dependence for most phosphor crystals has not yet been adequately established. This can be explained on one hand by the difficulty of measuring absorption in powders (usual state of phosphor crystals) and on the other hand by the existence for most such phosphor crystals of prolonged luminescence which may be a source of errors in measuring the yield of spontaneous luminescence.

Zinc oxide was selected because according to available literature (ref. 1) and according to our observations, it does not possess phosphoresence and, moreover, can easily be obtained in the form of thin semi-transparent films for which it is possible to measure absorption by attenuating the light which passes through it rather than by the scattering method which is usually used in studying powders. Thus, we decided to use ZnO because by using it we would better be able to measure the dependence in which we were interested than

*Numbers given in the margin indicate the pagination in the original foreign text.

were we to use other phosphor crystals.

EXPERIMENTAL PART

The quantum yield is the product of energy yield and the ratio between the wavelengths of the emitted and the absorbed light. The energy yield may be defined as the quotient obtained in dividing the emitted energy by the absorbed energy. In this way, for determining the nature of the dependence of yield on the wavelength, knowledge is needed of the laws of absorption and the change in the spectral composition of emission due to the length of the excitation wave. Special experiments were set up for the purpose of studying these problems.

Absorption was determined for ZnO films 10^{-4}--10^{-5}cm thick by measuring the attenuation in the light passing through them (ref. 2). It was demonstrated that in films of such thickness, wavelengths shorter than 385 mμ were completely absorbed. Apparently this holds true for layers of greater thickness.

Spectra of luminescence were studied for those same samples of zinc oxide for which the quantum yield was determined. The results obtained are shown in Figure 1. It is apparent that the spectral distribution of luminescence does not depend on the wavelength of the excitation light, at least for three wavelengths: 365, 312, and 254 mμ.

The yield of luminescence was determined for Kahlbaum zinc oxide. The samples on which measurements were taken consisted of layers of fine-crystalline powder $3 \cdot 10^{-3}$ g/cm^2 thick deposited from alcohol on cover glass. /1274 Samples of this thickness absorbed completely the excitation untraviolet and hardly attenuated the intensity of the luminescence passing through them. A PRK-4 light (a) (Figure 2) with a known spectral distribution of emission served at the source of excitation. Monochromatization of its light was done with a spectograph, b, in the focal plane of which was the cover glass, c, with the layer of oxide facing the excitation light.

On the surface of the sample we obtained an actual image of a mercury spectrum in the form of narrow luminescent bands, the brightness of which was measured by a Pulfrich photometer, d. The latter, by using the micrometer screw e, was set so that the band being measured with the photometer was in the center of the field of vision of the objective. A black screen, f, with a narrow slit allowing only one band to pass through, was glued to the cover glass. By shifting the sample, its location under the slit caused excitation of waves of different lengths. In this way in the field of vision of the photometer fell in turn the emission of one and the same location of the phosphor excited by different spectral lines. The fields of the photometer were equalized by changing the light flow of the standard (the electric light with a system of light filters).

Luminescence in the field of a mercury spectrum of 365-254 mμ was excited. Because of the fact that complete absorption corresponded to these wave lengths, the energy yield was determined as the ratio of the intensity of emission to the energy excitation incident on the phosphor. The ratio of the energy excitation and the excitation wave length was taken as the relative quantum yield. The results are shown in Figure 3. It is apparent that the relative quantum yield of luminescence of ZnO in the range of wave lengths of 365-254 mμ remains constant.

This result is similar to that obtained by S. I. Vavilov (ref. 3) and his school in measuring the yield of luminescence of phosphors (ref. 4).

EVALUATION OF RESULTS

We consider the luminescence of zinc oxide, according to measurements of its electrical and optical properties, to be attributable to the movement of electrons of the local level of atoms of the excess zinc to the primary zone. According to this concept the lack of dependence between the yield and λ seems natural since the probability of recombining electrons with the vacancies will hardly depend on the length of the light waves causing the occurrence of the latter. Despite this, we considered it necessary to set up ex- /1275 periments to show the lack of dependence of yield on the intensity of excitation for that range of intensities with which we dealt under the test conditions.

The fact of the matter is that the yield of luminescence of ZnO, remaining a constant value with greater intensities of excitation, begins to drop with small intensities (ref. 5). In order to show that with the excitation of ZnO by lines of a mercury spectrum of varying energy (the brightest of them of 365 mμ was eleven times more intense that the weakest of 330 mμ) the yield still did not depend on the intensity of excitation. A relationship was established between the brightness of luminescence, I, excited by waves of 365 and 254 mμ, and the energy of excitation, E. We took for initial intensities those with which we had been concerned in determining the spectral dependence of yield. Excitation was attenuated by the filters, g (Fig. 2), placed in front of the prism of the spectrograph.

The results of our measurements are shown in Figure 4. Here the linear dependence between I and E is shown by the dotted line. From Figure 4 it follows that with a attenuating in the intensity of a line of 365 mμ by a factor of ten the linearity between I and E is preserved (yield remains constant) and with greater attenuation in excitation the yield begins to drop (intensity of luminescence decreases faster than, proportionally, the intensity of excitation). The nature of the dependence of I on E is the same for both wave lengths (curves are parallel).

It was shown above that the intensity of the weakest excitation line was 9% of the energy of a line of 365 mμ. From Figure 4 it follows that even for it the yield still does not depend on the intensity of excitation. For brighter lines this is true to an even greater degree. In this way, the straight line shown by us in Figure 3 corresponds to the true dependence of relative quantum yield on the excitation wave length.

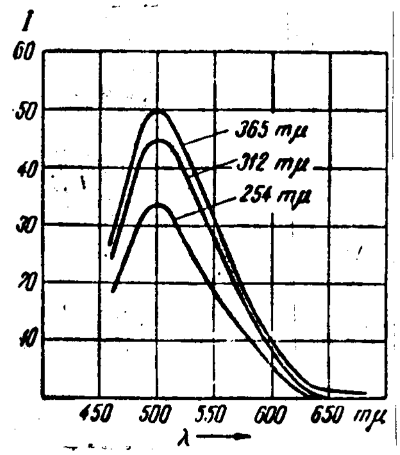

Fig. 1. **Spectra of luminescence of ZnO** excited by waves of different lengths.

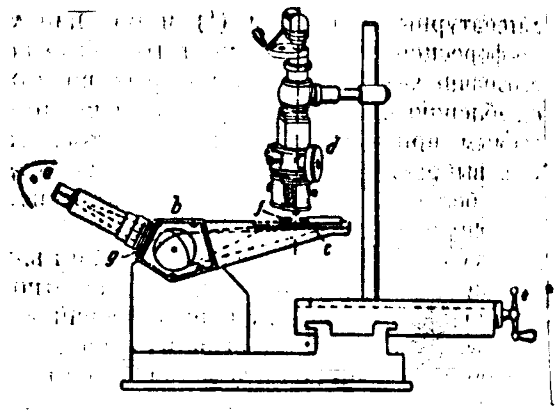

Fig. 2.

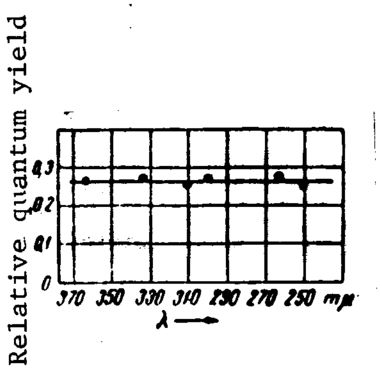

Fig. 3. Dependence of relative quantum yield of luminescence of ZnO on the length of excitation wave.

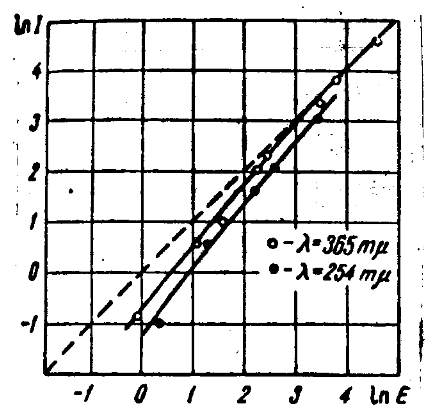

Fig. 4. Dependence of brightness of luminescence of ZnO on intensity of luminescence.

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